X-ray Diffraction Analysis of the Particulate Matter in Residual Oil Flyash

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ABSTRACT

X-ray diffraction studies are reported on a series of PM samples produced by combustion of residual fuel oil. The residual oil flyash (ROFA) from four oils of varying sulfur content were aerodynamically separated into <2.5 micron and >2.5 micron fractions using a cyclone. The analysis of their x-ray diffraction measurements indicated sharp lines due to the presence of crystalline components superposed on two broad peaks due to amorphous carbon. The intensity of the crystalline components tends to be higher in the <2.5 micron fractions and in oils with the higher sulfur content. The sharp lines have been identified with various sulfites and sulfates of Zn, V, Ni, Pb, Fe, Cu and Ca.

INTRODUCTION

Particulate Matter (PM) is composed of a mixture of particles directly emitted into the air and the particles formed in air from the chemical transformation of gaseous pollutants (secondary particles). The earlier focus of the US Environmental Protection Agency (EPA) was on the particulate matter less than 10 microns in diameter (PM_{10}). In July 1997, EPA adopted a new rule that, for the first time, addressed particulate matter with diameter less than 2.5 microns (fine PM or $PM_{2.5}$) [1]. The implementation of this new rule requires the acquisition of important scientific information regarding the effects of $PM_{2.5}$ on public health and welfare. These adverse health effects include premature mortality, aggravation of respiratory and cardiovascular symptoms and illness, change in lung structure, and altered respiratory defense mechanisms [2-4]. Two controversial studies (the Harvard University six-city study and the American Cancer Society study) have linked the presence of fine particular matter to premature mortality [5]. Generally, fine particles are considered to be more hazardous than coarse particles. Therefore, the analysis have to be done at molecular levels. In order to understand the molecular speciation and its parameters such as valency, solubility, acidity, and composition, it is essential to identify and analyze the elements and compounds present accurately by employing several analytical tools. Huffman et al., have carried out X-ray absorption fine structure (XAFS) analysis to investigate several elements in ROFA samples [6].

In this work, we have employed x-ray diffraction for the identification and analysis of the compounds present in $PM_{2.5}$ samples. The technique of x-ray diffraction allows identification of any crystalline material, elements or compounds, present in a sample. In this work, x-ray diffraction was used to investigate the suite of residual oil flyash (ROFA) samples separated aerodynamically into fractions <2.5 ($PM_{2.5}$) and >2.5 microns ($PM_{2.5+}$) in diameter. The ROFA samples were generated by combustion of residual fuel oil at the EPA laboratory at the Research Triangle Park in experiments conducted by Miller et al [7]. A series of eight samples were analysed. All the PM samples measured possess sharp lines superposed on two broad peaks. We could identify the sharp lines due to various sulfates of Zn, V, Ni, Pb Fe, Cu and Ca. The two broad peaks are due to presence of amorphous carbon [8].

EXPERIMENTAL

The combustion experiments were carried out in a North American three-pass fire tube package boiler, which is a practical, commercially available heavy fuel oil combustion unit. A detailed description of this boiler is given elsewhere [7]. Samples were

separated aerodynamically by a cyclone into fractions that were nominally < and > 2.5 microns in diameter, hereafter referred to as $PM_{2.5}$ and $PM_{2.5+}$. The sampling system consists of a large dilution sampler capable of isokinetically sampling 0.28m^3/mmin (10ft^3/min) of flue gas using a Source Assessment Sampling System (SASS) cyclone. The SASS cyclone produces 50 and 95% collection efficiencies at approximately 1.8 and 2.5 micron diameter, respectively. The resulting PM is collected on large (65 cm) Teflon coated glass fiber filters, transferred to sampling jars, and made available for analysis.

Although burnout was fairly complete (>99.7%), the inorganic content of the oils was quite low (0.02-0.10 wt.% ash), and the dominant element of the ROFA is carbon. Loss on ignition (LOI) measurements indicate that the carbon content of the $PM_{2.5}$ ranged from 64 to 87 wt.% and that of the $PM_{2.5+}$ from 88 to 97%. S content of the PM samples was ~ 1 to several wt.%, while the V content ranged from 0.5 to 5.9 wt.% and the Ni content from 0.08 to 0.8 wt.%. As reported in the paper by Miller et al. [7], the metals are typically more concentrated in the $PM_{2.5}$ samples than they are in the $PM_{2.5+}$ samples by factors ~3 to 6.

These samples were investigated using a Wide Angle X-ray Diffractometer (WAXD). The WAXD used is a Rigaku diffractometer (Model D/MAX) using Cu Kα radiation with a wavelength λ of 1.542 Å. The other experimental conditions include ½° divergence and scatter slits, 0.15mm receiving slits, step scans with 0.04° steps and 30sec, counting time at each step, and intensity measured in counts. This relatively slow scan process enabled us to obtain the diffraction pattern with resolved sharp lines due to various compounds. The analysis of the X-ray patterns have been carried out using Jade software package produce by MDI (Materials Data Inc.) and the JCPDS data files.

RESULTS AND DISCUSSION

The X-ray diffraction patterns of the two ROFA samples (oil #5) are shown in Figures 1 (<2.5 microns) and 2 (>2.5 microns). Figure 1 shows well defined sharp lines superposed on two broad peaks at $2\theta \equiv 26°$ and 44°) due to amorphous carbon[8]. The inorganic components have been identified as $CaSO_4$; $Zn_4SO_4(OH)_6 \cdot 5H_2O$; $Zn(SO_3) \cdot 2.5H_2O$; $VOSO_4$; $NiSO_4 \cdot 6H_2O$; PbS_2O_3; $Fe_3(SO_4)_4 \cdot 14H_2O$; $ZnSO_4 \cdot xH_2O$; $Ca(SO_4)(H_2O)_2$; Cu_2SO_4. All these phases are identified and labeled as shown in the Figs. 1, 2 and 3. Figure 2 shows only $CaSO_4$ phase and the two broad peaks due to carbon [7]. In a similar fashion a total of eight samples were analyzed and the inorganic phases identified are summarized in Table 1. The samples are found to contain various sulfates and sulfites of Zn, V, Ni, Pb, Fe, Ca and Cu. The intensities of the x-ray diffraction lines for these compounds is the largest for the ROFA samples obtained from the high sulfur No. 6 oil and for the $PM_{2.5}$ fraction of No. 5 oil (BL5FH). This is understandable since the high sulfur content would tend to produce higher levels of the sulfates. The other noticeable trend is the higher concentrations of the sulfates in the $PM_{2.5}$ fraction as compared to the $PM_{2.5+}$ fraction.

The major contribution of the present investigation using x-ray diffraction is that we have been able to identify various compounds and their water content in the ROFA samples. In making the identifications, we compared the diffraction patterns of all appropriate compounds available in the JCPDS files. Since the studies by Miller et al [7] had given the percentages of various elements present in these samples, our search was primarily confined to the various compounds of these elements. The information reported here on the various compounds should be useful for developing appropriate models for the formation of these compounds. Some of these compounds may have appropriate band gaps for the photocatalytic absorption of solar radiation [9]. In addition, some of these materials being acidic, may have the catalytic ability to crack hydrocarbons and create free radicals. Further work along these lines is needed to understand the harmful effects of $PM_{2.5}$. A more detailed description of our

investigations, including comparison with the findings obtained by other techniques, will be published elsewhere.

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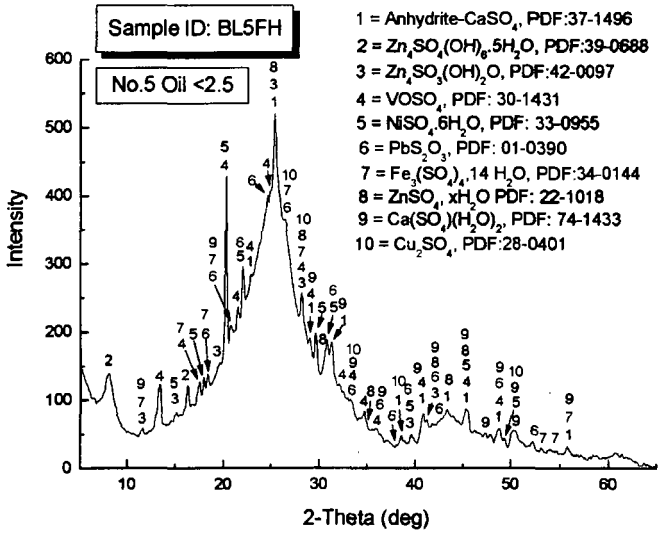

Fig. 1 Room temperature x-ray diffractogram of sample BL5FH. Lines due to various crystalline components are identified.

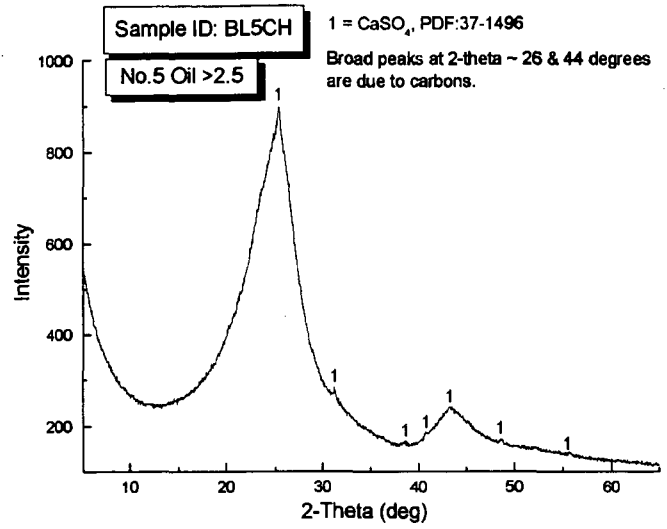

Fig. 2 Room temperature x-ray diffractogram of sample BL5CH. Lines only due to $CaSO_4$ are present. The broad peaks near $2\theta \sim 26°$ and 44° are due to amorphous carbons (see Ref. 8).

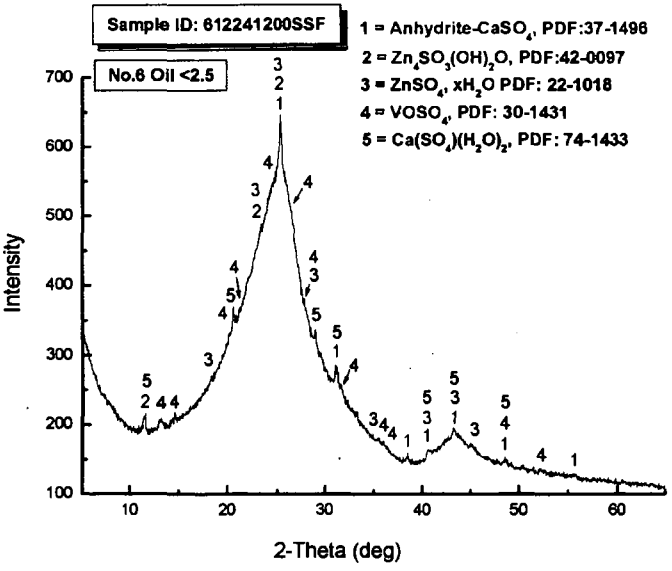

Fig. 3 Room temperature x-ray diffractogram of sample 612241200SSF. Lines due to various crystalline components are identified. The broad peaks are due to amorphous carbon.

Table 1: Identification of the compounds in the ROFA samples

Sample	Compound (PDF File)
BL5FH (#5 oil) <2.5	$CaSO_4$ (37-1496); $Zn_4SO_4(OH)6.5H_2O$ (39-0688); $Zn(SO_3).2.5H_2O$ (42-0097); $VOSO_4$ (30-1431); $NiSO_4.6H_2O$ (33-0955); PbS_2O_3 (01-0390); $Fe_3(SO_4)_4.14H_2O$ (34-0144); $ZnSO_4xH_2O$ (22-1018); $Ca(SO_4)(H_2O)_2$ (74-1433); Cu_2SO_4 (28-0401)
BL5CH (#5 oil) >2.5	$CaSO_4$ (37-1496)
701291400SSF (#6 oil) high sulfur <2.5	Same as BL5FH
70129400SSC (#6 oil) high sulfur >2.5	Same as BL5FH
612241200SSC (#6 oil) medium sulfur >2.5	$CaSO_4$ (37-1496); $Zn(SO_3).2.5H_2O$ (42-0097); $Ca(SO_4)(H_2O)_2$ (74-1433)
612241200SSF (#6 oil) medium sulfur <2.5	$CaSO_4$ (37-1496); $Zn(SO_3).2.5H_2O$ (42-0097); $ZnSO_4xH_2O$ (22-1018); $VOSO_4$ (30-1431); $Ca(SO_4)(H_2O)_2$ (74-1433)
701071200SSF (#6 oil) low sulfur <2.5	$CaSO_4$ (37-1496); $Zn(SO_3).2.5H_2O$ (42-0097); $VOSO_4$ $1.5H_2O$ (31-1444); $NiSO_4$ (34-0144); $Ca(SO_4)(H_2O)_2$ (74-1433)
807161300SSF baseline filter	$CaSO_4$ (37-1496); $VOSO_4$ (30-1431); $NiSO_4.6H_2O$ (33-0955); PbS_2O_3 (01-0390); $Fe(NO_3)_3.9H_2O$ (01-0124); $ZnSO_4xH_2O$ (22-1018); $Ca(SO_4)(H_2O)_2$ (74-1433); Cu_2SO_4 (28-0401); $NaAl(SO_4)_2.6H_2O$ (19-1186)